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The carbonate system geochemistry of shallow groundwater–surface water systems in temperate glaciated watersheds (Michigan, USA): Significance of open-system dolomite weathering

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ABSTRACT

We present here a field geochemical study of controls on carbonate weathering within rapidly circulating, shallow groundwater–surface water systems in the glaciated mid-continent region. Groundwaters and surface waters in three watersheds spanning the Upper to Lower Peninsulas of Michigan consist of Ca^{2+}-Mg^{2+}-HCO_3^- solutions derived from the open-system dissolution of calcite and dolomite in soils developed on mixed mineralogy glacial drift. The thermodynamic stabilities of calcite and dolomite both decrease with decreasing temperature, with dolomite more strongly affected. Thus, the low mean annual temperature of these temperate weathering environments maximizes the absolute solubility of dolomite as well as its solubility relative to calcite. Many groundwaters in the study area approach equilibrium with respect to the more soluble dolomite and are moderately supersaturated with respect to calcite. Groundwaters in each watershed have distinct and relatively narrow ranges of carbon dioxide partial pressure (P_{CO_2}) values, which increase significantly from north to south (log P_{CO_2} of –3.0 to –2.2 atm), suggesting that there are landscape-level differences in carbon transformation rates in soil weathering zones. Increases in weathering-zone P_{CO_2} values produce HCO_3^- concentrations that vary by a factor of five, but the Mg^{2+}/Ca^{2+} and Mg^{2+}/HCO_3^- ratios of all groundwaters are similar, suggesting relatively constant weathering input ratios of calcite and dolomite. Although surface waters commonly are between 2 and 10 times supersaturated with respect to calcite, the Mg^{2+}/HCO_3^- ratios of surface waters are very close to initial groundwater values, suggesting that back precipitation of calcite is not a significant process in these systems. The enhanced solubility of dolomite at low temperatures coupled with the landscape-level differences in carbon cycling suggest that temperate-zone weathering reactions in glaciated terrains are significant contributors to continent-scale fluxes of both Mg^{2+} and HCO_3^-.

Keywords: carbon, rivers, groundwaters, Michigan, carbonate saturation, dolomite dissolution, carbon dioxide.

INTRODUCTION

Weathering of carbonate and silicate minerals in the terrestrial near-surface environment plays a major role in regulating atmosphere and ocean chemistry on time scales of millions of years (e.g., Holland, 1978; Berner et al., 1983). Much of the weathering occurs in soils at the interface between the biosphere and the lithosphere, the site of rapid terrestrial organic matter production and degradation. The global riverine fluxes of Ca^{2+}, Mg^{2+}, and HCO_3^- are derived from both carbonate and silicate sources, and the relative contributions from each source are important for the long-term CO_2 cycle and ocean chemistry. On long time scales, Mg^{2+} added to the oceans via carbonate and silicate weathering may be removed by exchange for Ca^{2+} via basalt-seawater reaction (e.g., Hardie, 1996) or by dolomite formation (e.g., Holland and Zimmermann, 2000). Because the Mg^{2+} supplied to the oceans by rivers is not removed entirely as a carbonate, the input fluxes of HCO_3^- from the weathering of Mg-carbonates and Mg-silicates are not balanced by equivalent output fluxes of Mg-carbonates. Thus, the relative riverine inputs of Mg^{2+} from carbonate versus silicate sources bear significantly on the global carbon cycle.

On shorter time scales, the predicted response of terrestrial systems to global warming and atmospheric CO_2 increases is expected to include increases in biomass and in soil respiration rates. The terrestrial carbon reservoir has commanded increasing attention as the likely sink for anthropogenic CO_2 (Houghton et al., 1998, 1999). An increase in terrestrial biomass may result from the "fertilization" effect of elevated CO_2 levels on photosynthesis, with a large portion of this partitioned into below-ground biomass (e.g., Van Veen et al., 1991; Bowden et al., 1993). Plants grown in elevated CO_2 atmospheres have more rapid root and microbial respiration rates, which can increase CO_2 partial pressure (P_{CO_2}) values in soil gases (Hungate et al., 1997; Schlesinger et al., 2000; Andrews and Schlesinger, 2001; Williams et al., 2003). The increase in soil gas

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CO_2 may simply lead to an enhanced flux back to the atmospheric reservoir (e.g., Trumbore et al., 1996), or it may drive an increased carbon flux to the soil carbon pool and/or to groundwater systems as dissolved inorganic and organic carbon (e.g., Richter et al., 1995; Schlesinger, 1997; Williams et al., 2003).

Rapid equilibration of soil waters with carbonate minerals has been observed in experimental tree-growth chambers (Williams et al., 2003) and in natural shallow groundwaters (e.g., Freeze and Cherry, 1979; Reardon et al., 1979, 1980; Seifert, 1982; Van Breenan and Protz, 1988; Kempe et al., 1991; Ku, 2001). It is thus very important to understand the links between the rates of mineral weathering and organic matter dynamics in terrestrial settings. Via interaction with mineral solubilization, soil reactions police the rate of atmospheric carbon transfer from mid-latitude ecosystem reservoirs to hydrospheric reservoirs (groundwaters and oceans). Increased fluxes of dissolved inorganic carbon (DIC) and cations from mid-latitude areas also are important in terms of assessing changes to surface water compositions and for inputs to the global ocean reservoir. The annual global flux of dissolved carbon as DIC and dissolved organic carbon (DOC) from rivers has been estimated at ~0.6 Gt C/yr (e.g., Kempe, 1985; Kempe et al., 1991; Aumont et al., 2001), which is a small, but nontrivial, contribution to the global carbon budget.

Although there have been many studies of mineral weathering in surface environments, few have focused on the controls on carbonate equilibria in such systems or on the relative contributions of dolomite and calcite to weathering fluxes. Studies on solute fluxes from the terrestrial environment to the oceans via riverine discharge have focused primarily on the downstream reaches of major world rivers such as the Amazon, Yellow, and Mississippi Rivers (e.g., summary in Meybeck, 1987). The large drainage basins of these rivers integrate varying climates, lithology, soil compositions and depths, and land-use types, including agriculture, urban, and forest. Rates of chemical weathering and their implications for geochemical cycling over long time scales have been investigated (e.g., Blum et al., 1998; Huh et al., 1998; Jacobson et al., 2002; Millot et al., 2003). Others have focused on the internal riverine processing of trace elements and nutrients, isotopes (O, C, Sr) (Palmer and Edmond, 1992; Yang et al., 1996; Karim and Veizer, 2000), or the organic/inorganic speciation of carbon (Aucour et al., 1999; Roy et al., 1999; Telmer and Veizer, 1999; Finlay, 2003; Hélie et al., 2002; Barth et al., 2003).

The current fluxes of inorganic carbon from each continent are available from compilations of annual river-water discharge and DIC contents (e.g., Ming-hui et al., 1982; Kempe, 1985; Berner and Berner, 1996; Huh et al., 1998). Nearly 85% of the 0.6 Gt C/yr flux is derived from the Northern Hemisphere continents of Europe, North America, and Asia, all of which have significant areas of sedimentary bedrock and unconsolidated, glacially derived material (Holland, 1978; Meybeck, 1987). In general, the solubility of feldspars is very low, and dissolution rates are thousands of times slower than those of carbonate minerals (e.g., Holland, 1978; Amiotte Suchet and Probst, 1993; Berner and Berner, 1996; Roy et al., 1999). Rivers exclusively draining continental silicate regions tend to have very low HCO_3^- concentrations (i.e., <0.5 meq L^{-1} as HCO_3^-; Holland, 1978; Berner and Berner, 1996), whereas rivers draining carbonate-bearing areas, such as the Danube River in Europe and the Yellow River in China, tend to have higher overall HCO_3^- concentrations and HCO_3^- fluxes.

In North America, almost 90% of the HCO_3^- flux is derived from the mid-continent region, where the bedrock geology is dominantly sedimentary and mantled by carbonate-bearing glacial drift. It is this mid-continent region that we selected for an integrated study of surface water and groundwater geochemistry to better constrain landscape-level controls on carbonate weathering. Figure 1 is a schematic of the Mississippi and St. Lawrence River basin drainage, large portions of which are established atop landscapes that have been affected by repeated cycles of Pleistocene glaciation. Given the rapid reaction rates of carbonate minerals, the chemistry of such drainage systems is likely to be quite sensitive to short-term changes in the carbon cycle. According to Raymond and Cole (2003), there appeared to be a significant increase in the alkalinity flux from the Mississippi drainage system during the past half-century, an increase they attribute to enhanced fluxes from agriculturally dominated watersheds. This is consistent with data on soil CO_2 contents and fluxes (Reardon et al., 1979; Brook et al., 1983; Buyanovsky and Wagner, 1983; Solomon and Cerling, 1987; Lee, 1997; Andrews and Schlesinger, 2001), which show that soil gas CO_2 profiles are generally controlled by depth variation in rates of microbial and root respiration and diffusive transport.

Early studies of the thermodynamic controls on the carbonate geochemistry of near-surface waters primarily focused on the role of CO_2 partial pressure on calcite solubility, rather than temperature, as the most important variable (e.g., Brook et al., 1975; Harmon et al., 1975; Drake and Wigley, 1975; Trainer and Heath, 1976; Drake, 1983). However, another important control on carbon fluxes is the inverse temperature dependence of carbonate mineral thermodynamic stability. The stability of both dolomite and calcite decreases with decreasing temperature, but the temperature effect is stronger for dolomite, which has an equilibrium stability constant that is more strongly dependent on temperature (e.g., Langmuir, 1997; Sherman and Barak, 2000; Hyeong and Capuano, 2001). Using the most recently compiled thermodynamic data for dolomite (e.g., Hyeong and Capuano, 2001), the equilibrium constant for dolomite becomes progressively greater than that of calcite as temperatures decrease below ~30 °C (Fig. 2A). Considering a solution at 10 °C and a Mg^{2+}/Ca^{2+} molar ratio of 0.5, the solubility of calcite versus dolomite at various P_{CO_2} values, in terms of HCO_3^- total concentration, is significantly enhanced relative to pure calcite (Fig. 2B; after Williams et al., 2003).

The Michigan landscape provides an excellent natural laboratory in which to examine controls on groundwater and surface water geochemistry and the limitations they impose on carbonate weathering intensities. In order to better understand the fundamental controls on these fluxes, we investigated the carbonate mineral equilibria and dissolution-precipitation mass balances in watersheds developed on Pleistocene glacial drift deposits, many of which are carbonate-bearing. We integrated data on the carbonate geochemistry of surface waters and groundwaters in three Michigan watersheds, the Tahquamenon, the Cheboygan, and the Huron, located along an environmental gradient (locations shown in Fig. 3). Catchment topography is dominated by upland moraine systems, which control drainage divides on both regional and local watershed scales. Close chemical linkages between groundwater and surface water systems have been forged by the high permeability of soils and underlying glacial drift across the state (Bent, 1971; Mandle and Westjohn, 1989; Rheaume, 1991; Holtschlag, 1996; Grannemann et al., 2000). The vast majority of groundwaters discharge into the Great Lakes catchment, with <2% of meteoric water discharging into the deeper basinal-scale flow system (Eberts and George, 2000).

HYDROGEOLOGIC FRAMEWORK OF FIELD STUDY SITES

In designing our field study, we considered differences in glacial history, drift and bedrock lithology, as well as temperature, geochemical and ecological gradients. Accordingly, we selected three watersheds in the state of Michigan for comparative investigation: the Tahquamenon watershed in the Upper Peninsula, the Cheboygan watershed in the northern Lower Peninsula,

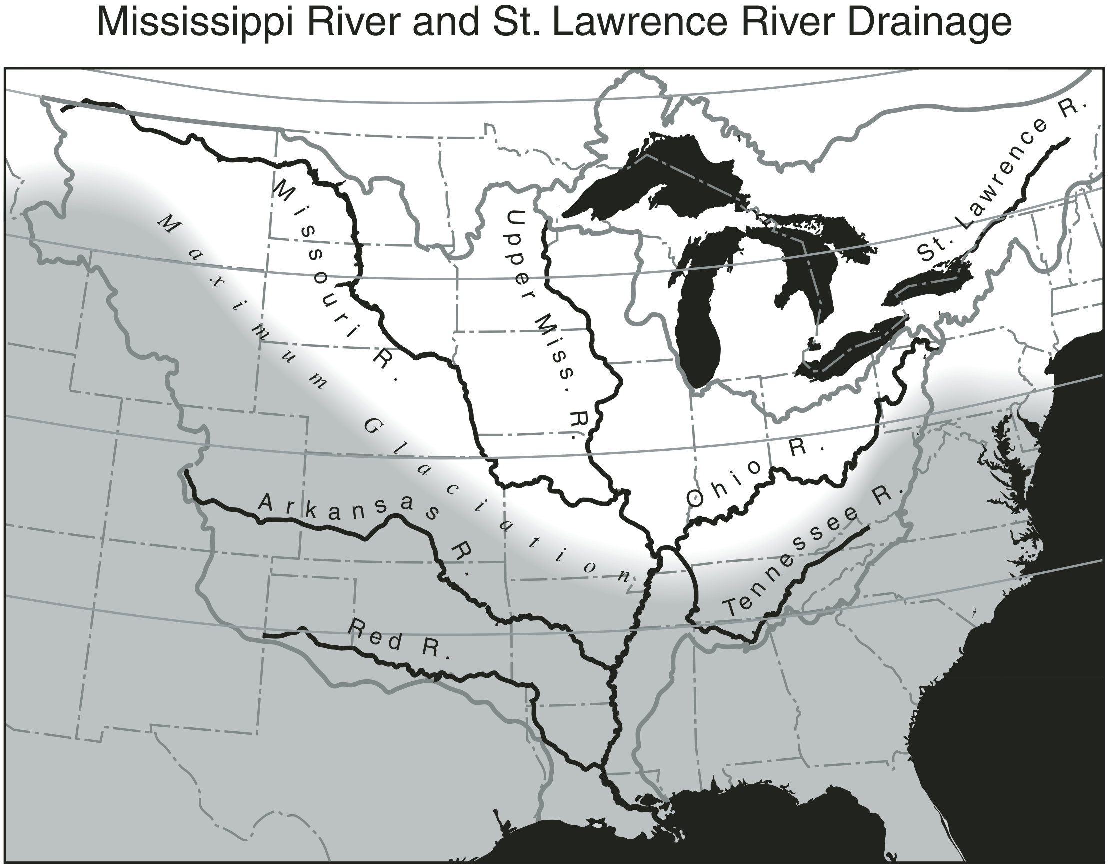

Figure 1. Hydrological regions of central North America showing the St. Lawrence and Mississippi River drainages. The significant regional extent of Pleistocene glaciation on these two major drainages is shown schematically.

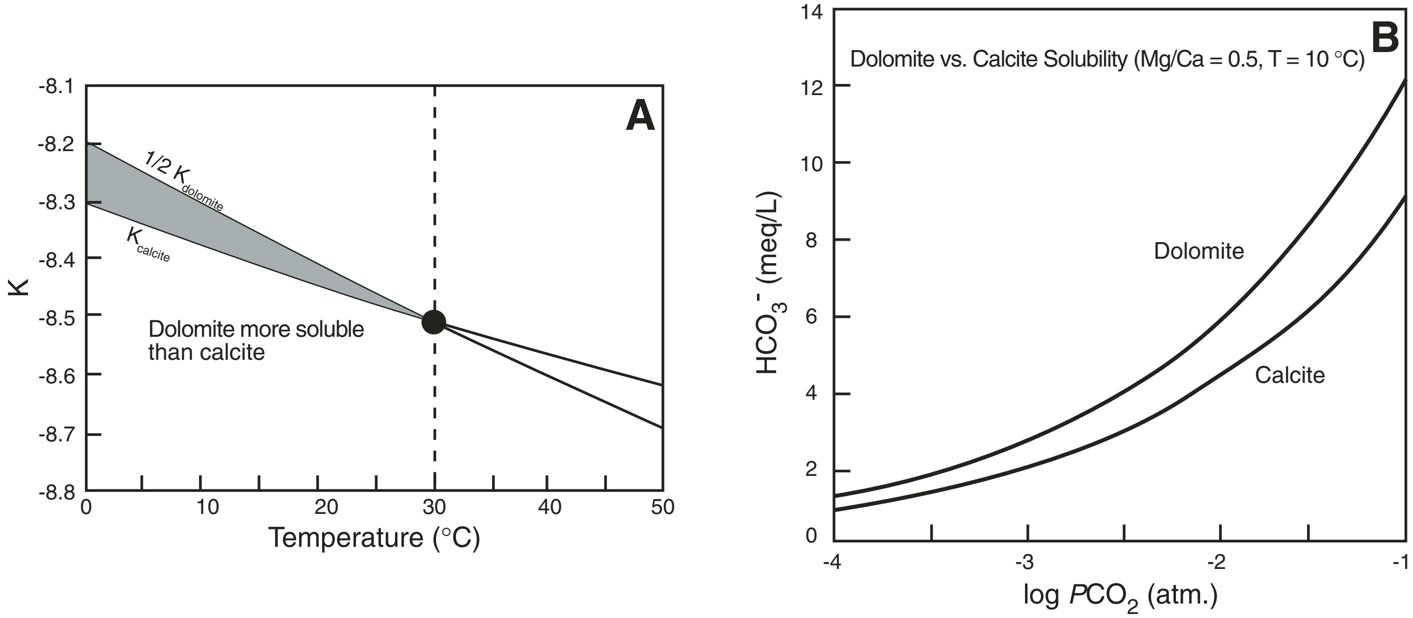

Figure 2. Relevant stability data for calcite versus dolomite. (A) Dolomite and calcite thermodynamic data ($K_{calcite}$ and ½ $K_{dolomite}$) as function of temperature showing that the equilibrium constant value for dolomite increases more significantly with decreasing temperature than does the equilibrium constant value for calcite (after Langmuir, 1997). (B) Solubility at 10 °C, in terms of HCO_3^- total concentration of pure calcite versus dolomite in a solution with Mg^{2+}/Ca^{2+} molar ratio of 0.5 at various values of CO_2 partial pressure (after Williams et al., 2003).

and the Huron watershed in southeastern Lower Peninsula. The general framework of these mid-continent surficial aquifer systems and drainage basins is shown in Figures 3A, 4A, 4B, and 4C. The Tahquamenon drains into Lake Superior, and the Cheboygan and the Huron drain into Lake Huron and Lake St. Claire, respectively, and all are part of the St. Lawrence–Great Lake drainage system. The significant latitudinal gradient represented by our study sites leads to differences in mean annual temperature, which ranges from a low of 4.8 °C in the Tahquamenon watershed, to 10.0 °C in the Huron watershed near Ann Arbor.

Glacial drift deposits commonly contain carbonate minerals reworked from underlying bedrock formations during the multiple glacial advances and retreats. Soil development over the past 6000–12,000 yr has led to accumulation of organic carbon at greatly accelerated rates relative to nonglaciated landscapes (Harden et al., 1992). Largely unaltered parent material is typically encountered within 1–3 m of the surface. Dissolution of carbonate minerals may be enhanced in glacial drift deposits due to the grinding and stress induced by glacial actions (e.g., Sharp et al., 1995, 1999; Anderson et al., 2000). Carbonate dissolution profoundly affects soil solution pH, soil profile development, metal hydroxide distributions, and solute fluxes to groundwaters (Reardon et al., 1980; MacDonald et al., 1991, 1992). These geochemical relations contrast sharply with those of the more intensively studied carbonate-poor landscapes that dominate the eastern and southern regions of the United States (e.g., Likens and Bormann, 1995; Richter et al., 1995; Lee, 1997).

Like much of the adjacent mid-continent region, the study watersheds were developed atop variable thicknesses of glacial drift deposited in the waning stages of the last glacial advance. Thicknesses of up to 300 m are not uncommon, and many groundwater supply wells in Michigan tap glacial drift aquifers (e.g., Rheaume, 1991). The timing of glacial retreat varies across the watersheds: the Huron watershed was established on drift deposits ca. 18 ka in age, while the Cheboygan and Tahquamenon watersheds in the northern Lower and Upper Peninsula of Michigan are only ca. 11 ka in age (e.g., Futyma, 1981). The drift deposits overlie Paleozoic bedrock units of variable lithology, permeability, and porosity (see Fig. 3B). In brief, carbonate rocks are most abundant in the Silurian-Devonian sections, which have subcrops located along the northern and southern rims of the Michigan Basin. These carbonates are commonly interbedded with evaporite minerals and consist of both calcite and dolomite interbeds (e.g., Catacosinos et al., 1990). Thus,

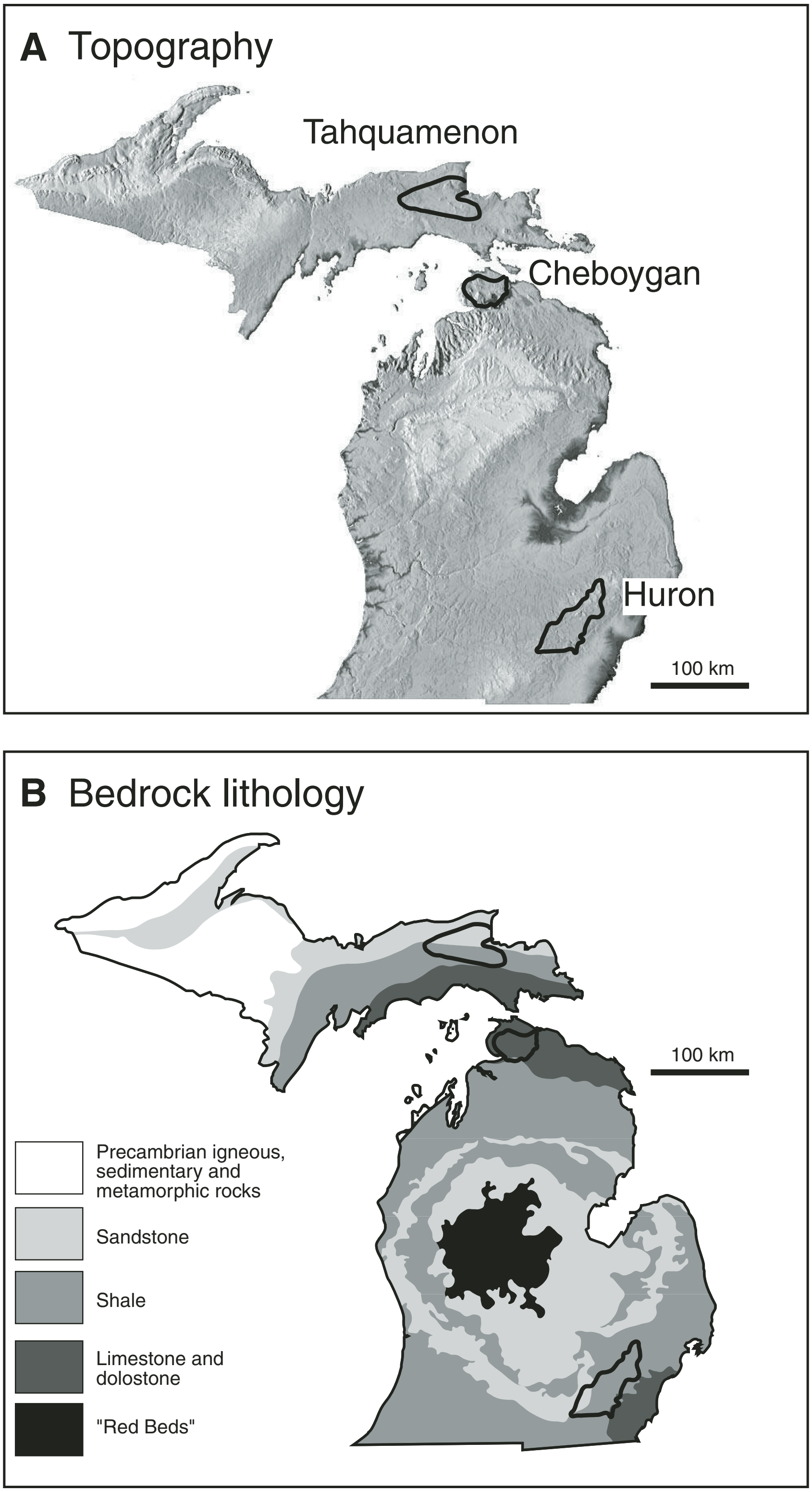

Figure 3. Location maps of watershed study sites in the state of Michigan with the study watersheds indicated by shading: the Tahquamenon (Upper Peninsula), the Cheboygan, and the Huron watersheds from north to south. (A) Shaded relief map, with topography generally controlled by variation in thickness of glacial deposits. (B) Subcrop bedrock lithology under Pleistocene glacial deposits. "Red Beds" includes multiple Jurassic terrestrial and marginal marine sedimentary deposits that consist mainly of sandstone, shale, and clay, with minor beds of limestone and gypsum.

glacially reworked sediments throughout the Lower Peninsula of Michigan commonly contain both carbonate minerals, as has been demonstrated by studies of drift soil mineralogic profiles (Schaetzl, 1992; Jin, 2007).

The Tahquamenon watershed has very subdued topography and largely represents slow drainage from wetlands established atop thin, quartz-rich glacial drift. The glacial drift mantles sandstones of Proterozoic and Cambrian age and Ordovician shales that represent the base of the Michigan Basin stratigraphic section. The Cheboygan and Huron watersheds have much more dramatic topography due to thick moraine deposits in these areas. Carbonate mineral content of the glacial drift in the Cheboygan and Huron watersheds is much higher than in Tahquamenon, and it affects the watershed solution chemistry and soil profile development. Results from previous hydrogeochemical studies of Michigan surface water chemistry suggest that there are fundamental differences in surface water chemistry among these watersheds (Rheaume, 1991).

For the Tahquamenon watershed, the mean annual temperature is 4.8 °C, and the average annual precipitation is 82 cm (NOAA, 1992). The Quaternary sediments in the Tahquamenon watershed are thin (<15 m) and are mainly composed of lacustrine organic and clay deposits with some ice-contact moraines, including sands and silts. The underlying bedrock geology is dominantly shale and sandstone (see Fig. 4B). The watershed has an ~100 d growing season, and vegetation is dominated by white-red pine and Jack pine forests, some northern hardwoods, and pasture land and limited crops (Albert, 1995).

The Cheboygan watershed has a mean annual temperature of 5.5 °C, and the average annual precipitation is 84 cm (NOAA, 1992). Glacial deposits range between 15 and 180 m thick in the watershed. Thick deposits of highly permeable lake beach sands form the floor of the watershed as a result of highstands of the Great Lakes (Farrand, 1982), while sandy glacial till forms the highlands. The Cheboygan watershed has the thickest glacial deposits of the three watersheds, and as a result, the greatest relief. The bedrock geology underlying the glacial deposits is Devonian-Silurian limestones and dolostones (see Fig. 3B). The watershed has a growing season of 100 d, and the dominant land use is northern hardwood forests and pasture (Albert, 1995).

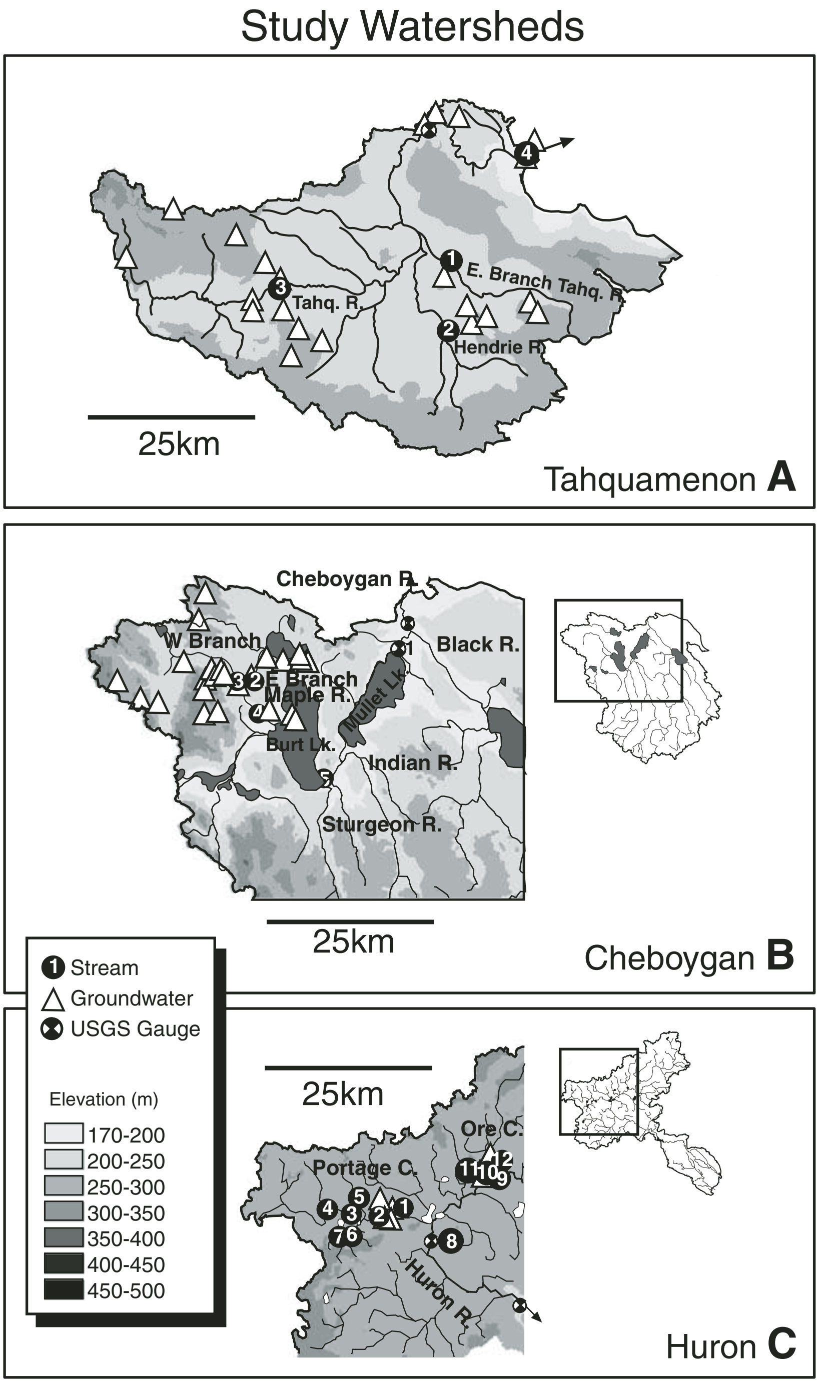

Figure 4. Watershed drainage map sketches for each of the three study watersheds with approximate groundwater locations and surface water locations indicated. Groundwater locations are shown in closed circles, and surface water locations are shown in open triangles. (A) The Tahquamenon watershed. (B) The Cheboygan watershed. (C) The Huron watershed.

The Huron watershed has a mean annual temperature of 10.0 °C, and the average annual precipitation is 85 cm (NOAA, 1992). The glacial deposits are primarily contact features including ground moraines and kames with some outwash. The moraines are composed of silts, sands, and gravels, while the outwash is mostly sorted sands and gravels (Farrand, 1982). The Quaternary sediment is variable in thickness (<15–122 m) and is inhomogeneous, containing lenses of material of differing permeability. The bedrock geology underling the Huron watershed is primarily Devonian shales, with sandstone along the eastern edge (see Fig. 4C). Studies on carbonate precipitation (Szramek and Walter, 2004) and arsenic mobility (Szramek et al., 2004) have been conducted on the Huron watershed. The

Huron watershed has a growing season of 140–150 d, and oak-hickory and beech-sugar maple forests dominate the vegetation. The longer growing season allows for extensive croplands rather than pastures (Albert, 1995).

METHODS

Field Sampling

Sampling in the three watersheds was conducted between 1997 and 2004. Groundwater was collected in summer 2000 and late fall 2003 in the Tahquamenon, in fall 1997, 2000, and spring 2003 in the Cheboygan, and in fall 2000, 2001, and spring 2001 and 2002 in the Huron watershed. Surface water samples from the three watersheds were collected seasonally (early spring through fall) to capture annual variations in chemistry. The Tahquamenon streams were sampled during 2000–2003, the Cheboygan in 1997–2003, and the Huron in 1999–2001 and in 2003. Stream sampling locations for each watershed are shown in Figures 4A–4C. At sampling sites, stream waters were collected upstream of large roads and developments to limit potential contamination from local runoff. About 240 surface water samples were taken in total. Groundwater was collected from household and small business wells that tap shallow Quaternary aquifers. Data from drillers' logs (depth, subsurface geology, static water level) were used to guide selection of wells for sampling. About 75 groundwater samples were obtained from the three watersheds.

Temperature, conductivity, and pH for each sample were determined in the field. Temperature was measured using a YSI model 58 meter and a YSI 5239 probe with high-sensitivity membranes directly at the source, either in the stream or at the groundwater well in the flow stream. Conductivity was measured using a Corning 316 meter to provide a rapid geochemical reference point, with a precision of ±5%. A Corning 315 high-sensitivity pH meter with an Orion Ross combination pH electrode was calibrated with low ionic strength buffers of 4.10 and 6.97 (corrected for temperature) and used to measure pH in the field as close to the water temperature as possible. Because the pH of a sample can change due to degassing and warming, samples were placed in a large-volume airtight container and measured at least twice to ascertain electrode stability. The reproducibility of field pH determinations was ±0.02 pH units.

Sample aliquots for later chemical analysis in the laboratory were field-filtered through a 0.45 μm nylon filter into their respective bottles and kept cold until analyzed. Acid-washed high-density polyethylene (HDPE) bottles were used to collect cation aliquots. HDPE bottles cleaned with purified water were used to collect alkalinity and anion samples. Double deionized water–washed glass serum bottles were used to store samples for DIC analysis. DIC samples were poisoned in the field against biological activity using $CuCl_2$ and were filled to the top with no headspace before capping. Cation aliquots were preserved in the field with ultrapure HNO_3.

Laboratory Analyses

Major-element chemistry was measured by inductively coupled plasma–atomic emission spectroscopy (ICP-AES) for cations and ion chromatography (IC) for anions on several different instruments, due to laboratory equipment upgrades. Prior to 2002, a Leeman Labs, Inc., Plasma-Spec ICP-AES 2.5 was used to analyze Ca^{2+}, Mg^{2+}, Na^+, K^+, Sr^{2+}, Ba^{2+}, Mn^{2+}, $Fe^{2+/3+}$, Zn^{2+}, H_4SiO_4, and B with a precision of ±2% for major and ±5% for minor elements. Samples from 2002 were analyzed on a Perkin Elmer Optima 3300 DV, and samples from 2003 were analyzed on a Jobin Yvon Horiba Ultima 2C. Analytical precision was ±4% on the Leeman ICP and ±2% on the Perkin Elmer and Jobin Yvon Horiba instruments. Anions (F^-, Cl^-, SO_4^{2-}, and NO_3^-, F^-, and Br^-) were analyzed on a Dionex 4000I series ion chromatograph (IC) with an AS14 column prior to 2002 and a Dionex ICS-2500 IC in 2002–2003. Analytical precision was ±3% on the 4000I series IC and ±2% on the 2500 series IC. Reanalysis of several ICP and IC samples on the new instruments yielded results consistent with previous measurements, within analytical precision. Br^- and F^- were consistently below detection and were excluded from the results table. Samples gathered for DIC ($= H_2CO_3^0 + HCO_3^- + CO_3^{2-}$) were analyzed on a UIC Coulometrics CO_2 coulometer with a precision of ±2%. Titration alkalinity (here largely equal to carbonate alkalinity, $HCO_3^- + 2CO_3^{2-}$) was measured by electrometric endpoint titration using a Radiometer TitraLab automated titration system. Due to the given measurement precision (±0.01 meq/kg) and the pH range of the samples, the carbonate alkalinity was equivalent to the concentration of HCO_3^-. Charge balance calculations were always within ±5%. The measured DIC and titration alkalinity measurements of the samples agreed well within the precision of the two measurements, suggesting that the CO_2 system was well constrained and consistent among the three carbonate system parameters measured (e.g., pH, DIC, and titration alkalinity).

Thermodynamic Modeling and Aqueous Speciation

Aqueous speciation and mineral ion activity products (IAPs) were determined using the U.S. Geological Survey (USGS) program SolminEQ.88 (Kharaka et al., 1988). The carbonate system parameters used were usually carbonate alkalinity and pH, although results with DIC and pH were cross-compared to determine internal consistency. Values for P_{CO_2}, IAP/$K_{calcite}$ (Ωcal), and $IAP_{dolomite}$ were obtained from the SolminEQ.88 output. As discussed by Drever (1997), the normalized saturation state ratio concept from Zhang and Nancollas (1990) was used to compare the IAP of dolomite [$CaMg(CO_3)_2$] on the same molar basis as that of calcite ($CaCO_3$). This was accomplished by taking the square root of $IAP_{dolomite}$ from SolminEQ.88.

This normalized $IAP_{dolomite}$ value was compared to the ½ log $K_{dolomite}$ (equilibrium constant) value (−8.45) at 25 °C (Hyeong and Capuano, 2001) to obtain $\Omega_{dolomite}$ for sedimentary dolomite of intermediate ordering. Given a precision of ±0.02 pH units and the uncertainty in the titration alkalinity, the uncertainty in P_{CO_2} was calculated to be ~10%. The error in Ω for calcite and dolomite was within 25% as determined by the precisions of the carbonate input parameters (DIC, alkalinity, pH).

RESULTS AND INTERPRETATIONS

Complete geochemical databases for the field, laboratory, and calculated parameters for groundwaters and surface stream waters are presented in Appendixes 1 and 2, respectively.[1] Averaged data are presented in Table 1 for groundwater samples and in Table 2 for surface stream water samples.

Elemental Stoichiometries and Mineral-Water Reactions

The groundwaters within these shallow glacial drift aquifers acquire solutes from the dissolution of minerals in the soil zone. As shown in Figure 5A, groundwater samples from each of the three watersheds are dominantly HCO_3^-, Ca^{2+}, and Mg^{2+} waters, and they fall close to a 2:1 line, which is consistent with the ratio obtained by dissolving carbonate minerals with carbonic acid ($Ca^{2+} + Mg^{2+}$: 2 HCO_3^-). Groundwaters from all three watersheds have an average ($Ca^{2+} + Mg^{2+}$):

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[1] GSA Data Repository item 2007059, detailed groundwater and surface water geochemistry data from the Tahquamenon, the Cheboygan, and the Huron watersheds, is available on the Web at http://www.geosociety.org/pubs/ft2007.htm. Requests may also be sent to editing@geosociety.org.

TABLE 1. GROUNDWATER GEOCHEMISTRY

Watershed	Value	pH	T (°C)	Alk (meq/L)	$Ca^{2+} + Mg^{2+}$ (m*M*)	Mg^{2+}/HCO_3^-	Mg^{2+}/Ca^{2+}	Log PCO_2 (atm.)	$(IAP/K)_{dol}$	$(IAP/K)_{cal}$
Tahquamenon	Average	8.07	8.7	2.42	1.28	0.18	0.53	–2.96	0.96	1.42
(*n* = 21)	Median	8.08	8.4	2.47	1.28	0.19	0.51	–2.95	0.98	1.40
	STD	0.32	2.0	0.60	0.44	0.03	0.12	0.36	0.43	0.62
Cheboygan	Average	7.71	9.0	3.54	1.90	0.21	0.64	–2.45	0.65	1.07
(*n* = 28)	Median	7.74	8.7	3.58	1.80	0.20	0.63	–2.52	0.66	1.05
	STD	0.19	2.5	0.90	0.50	0.03	0.08	0.30	0.17	0.29
Huron	Average	7.59	11.3	5.31	2.77	0.17	0.51	–2.13	1.46	1.91
(*n* = 22)	Median	7.61	11.1	5.37	2.71	0.17	0.50	–1.95	1.35	1.85
	STD	0.12	0.9	0.30	0.31	0.01	0.05	0.13	0.39	0.45

Note: Alk—alkalinity, IAP—ion activity product, STD—standard deviation, K—equilibrium constant, dol—dolomite, cal—calcite.

TABLE 2. SURFACE WATER GEOCHEMISTRY

Watershed	Value	pH	*T* (°C)	Alk (meq/L)	$Ca^{2+} + Mg^{2+}$ (m*M*)	Mg^{2+}/HCO_3^-	Mg^{2+}/Ca^{2+}	Log PCO_2 (atm.)	$(IAP/K)_{cal}$
Tahquamenon	Average	7.54	12.77	1.18	0.71	0.20	0.47	–2.76	0.54
(*n* = 42)	Median	7.62	11.10	1.22	0.76	0.20	0.46	–2.73	0.12
	STD	0.51	8.19	0.56	0.29	0.05	0.08	0.37	0.83
Cheboygan	Average	8.17	12.36	2.84	1.54	0.20	0.59	–3.00	3.27
(*n* = 138)	Median	8.21	12.85	2.96	1.60	0.20	0.58	–3.01	2.81
	STD	0.30	6.90	0.45	0.27	0.02	0.11	0.26	2.50
Huron	Average	8.15	16.77	4.07	2.68	0.23	0.52	–2.22	7.37
(*n* = 66)	Median	8.20	19.65	3.96	2.62	0.22	0.51	–2.74	6.00
	STD	0.28	7.19	0.56	0.42	0.05	0.10	1.24	5.00

Note: Alk—alkalinity, IAP—ion activity product, STD—standard deviation, K—equilibrium constant, cal—calcite.

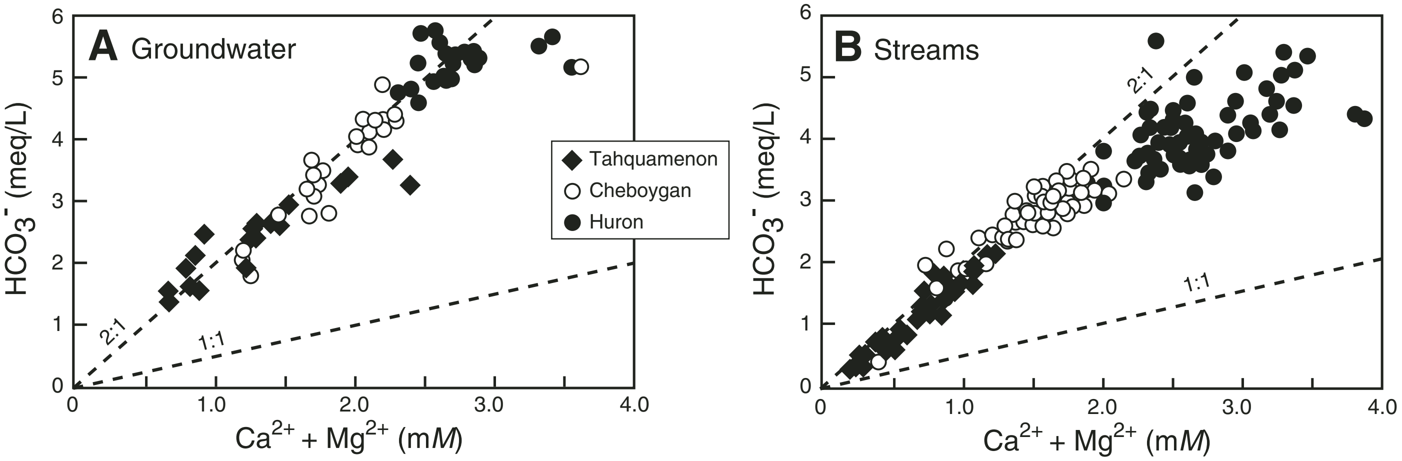

Figure 5. $Ca^{2+} + Mg^{2+}$ versus HCO_3^- relationships for groundwater (A) and surface streams (B) within the three study catchments. The groundwaters for the three watersheds fall close to the 2:1 line ($2HCO_3^- = Ca^{2+} + Mg^{2+}$), and no significant difference between the groundwaters is observed according to a $(Ca^{2+} + Mg^{2+})/HCO_3^-$ ratio of 0.51 ± 0.01. This strongly indicates that the groundwater chemistry is controlled by carbonic acid dissolution of calcite and dolomite present in the glacial drift.

HCO_3^- ratio of 0.53 ± 0.06, indicating no significant difference in their relative solute distributions. Groundwaters from the Huron watershed have the highest alkalinity values (mean HCO_3^- concentration of 5.31 ± 0.30 m*M*), whereas groundwaters from the Tahquamenon watershed have much lower alkalinity values (mean HCO_3^- concentration of 2.42 ± 0.60 m*M*), less than half those of the Huron watershed. These watershed-scale differences suggest that carbonate mineral solubility within each watershed may be controlled locally by factors such as climate, abundance of carbonate, soil thickness, and physical aquifer characteristics.

The major solute composition of surface waters in these watersheds, shown in Figure 5B, is influenced by contributions from groundwater, precipitation, runoff from anthropogenic sources, and in-stream or lake processes. Shallow glacial drift groundwater influx, however, is the major source of water and solutes to these surface systems, as can be seen from the similarity between groundwater and surface water major-element chemistries (compare groundwaters and streams

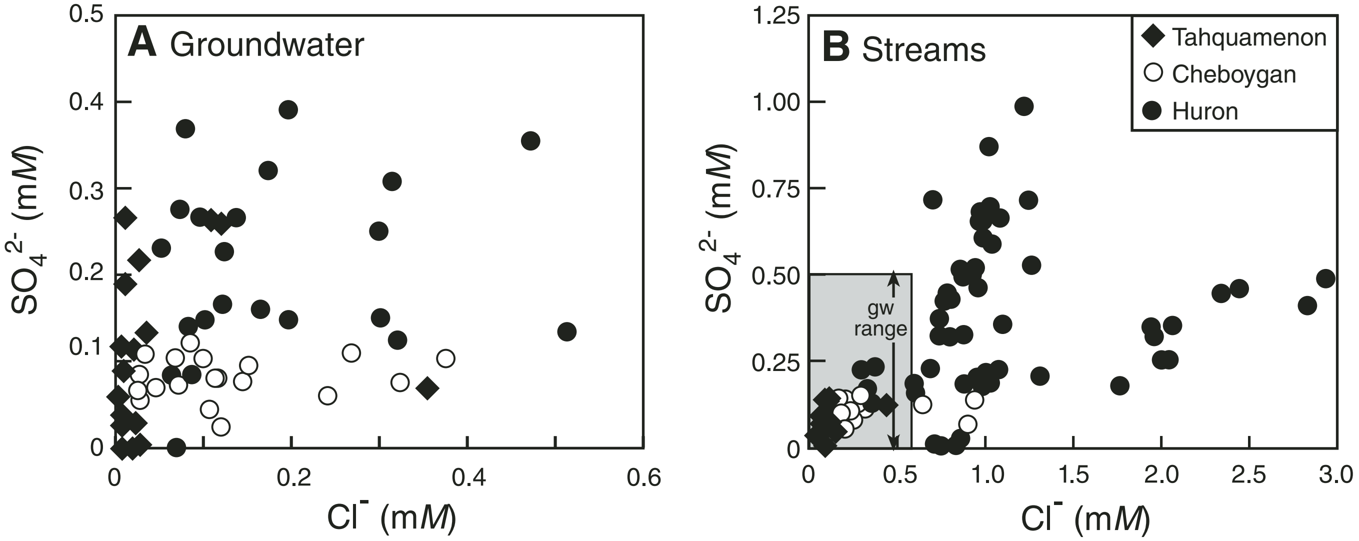

Figure 6. SO_4^{2-} versus Cl^- anion relationships for groundwaters (gw) (A) and surface streams (B) within the three study catchments. The Tahquamenon watershed has higher SO_4^{2-} to Cl^- ratios than do the Huron and Cheboygan watersheds. The Huron watershed has particularly elevated Cl^- concentrations in surface waters due to anthropogenic inputs from road de-icing salts.

in Fig. 5). The relationship between HCO_3^- and Ca^{2+} + Mg^{2+} concentrations in surface waters again indicates a stoichiometry consistent with carbonate mineral dissolution by carbonic acid. The composition of the surface waters of the Tahquamenon and Cheboygan watersheds falls close to the 2:1 line, similar to their respective groundwaters, but surface waters are generally more dilute. The Huron surface waters, unlike the Huron groundwaters, however, lie below the 2:1 line, indicating a relative increase in Ca^{2+} and/or Mg^{2+} relative to HCO_3^-.

This imbalance in the divalent cation to bicarbonate chemistry of the surface waters in the Huron watershed is largely due to the input of anthropogenic salts, such as $CaCl_2$ and NaCl, which contribute Cl^- and possible sulfide oxidation to produce SO_4^{2-}. Although groundwaters from each watershed contain significant amounts of Cl^- and SO_4^{2-} (see Fig. 6A), these are generally well below 0.5 m*M*. The Tahquamenon groundwaters have higher SO_4^{2-} than Cl^- (SO_4^{2-}/Cl^- of 2.5 to 8), whereas the Huron and Cheboygan groundwaters in general have a SO_4^{2-}/Cl^- ratio of less than 1. The SO_4^{2-} and Cl^- concentrations of the surface stream waters are also shown in Figure 6B. For the Tahquamenon and Cheboygan watersheds, surface waters have a very similar range of SO_4^{2-} and Cl^- concentrations to those of their source groundwater values. In contrast, the surface waters of the Huron watershed have markedly higher Cl^- and SO_4^{2-} concentrations than the source groundwaters, with surface water concentrations of Cl^- ranging between 0.3 and 3.0 m*M* and SO_4^{2-} generally between 0.02 and 1.0 m*M*. The majority of Huron surface waters have low SO_4^{2-}/Cl^- ratios, much less than 1. The Huron watershed experiences considerably more anthropogenic pollution than do the other two watersheds, and the large input of Cl^- to surface waters is derived from de-icing salts and water softeners (e.g., Jones and Sroka, 1997). As discussed by Szramek and Walter (2004), the Cl^- from anthropogenic salts is charge balanced by both Na^+ and Ca^{2+} in the surface waters of the Huron watershed, which produces the excess divalent cation concentrations relative to HCO_3^- shown in Figure 5B.

The relative proportions of Mg^{2+} and Ca^{2+} in the groundwater and surface waters of the three watersheds are shown in Figures 7A and 7B, respectively. While Ca^{2+} is a product of the weathering of both calcite and dolomite, Mg^{2+} is derived mainly from dolomite in the lower Paleozoic carbonate material found in the Michigan Basin. The Mg^{2+}/Ca^{2+} ratios of groundwaters and surface waters are similar in the three study watersheds. Groundwaters of the Tahquamenon, Cheboygan, and Huron watersheds have average Mg^{2+}/Ca^{2+} ratios of 0.53 ± 0.12, 0.64 ± 0.08, and 0.51 ± 0.05, respectively (see summary of averages in Table 1). Similarly, surface waters had average ratios of 0.47 ± 0.08, 0.59 ± 0.11, and 0.52 ± 0.10, respectively (see summary of averages in Table 2). The Mg^{2+}/Ca^{2+} mole ratios for groundwaters and surface waters shown in Figure 7 always exceed a value of 0.3 and are generally less than a value of 0.75.

When considering calcite and dolomite molar formulas normalized to CO_3^{2-}, a solution Mg^{2+}/Ca^{2+} ratio of 0.33 would be attained by dissolving nearly equal amounts by weight of calcite and dolomite (one mol Ca^{2+} from calcite plus 0.5 mol Ca^{2+} from dolomite, and 0.5 mol Mg^{2+} from dolomite). Similarly high Mg^{2+}/Ca^{2+} ratios have been observed in surface waters and groundwaters from other carbonate weathering environments, most recently in a very thorough study of solute sources and ion exchange processes of the Bow River in southern Alberta (Grasby and Hutcheon, 2000). Here, elevated Mg^{2+}/Ca^{2+} ratios were interpreted as evidence for smectite ion exchange reactions, even though dolomite dissolution is the dominant source of Mg (Grasby et al., 1999). In contrast, kaolinite is the dominant secondary aluminosilicate in soil profiles of the three Michigan watersheds (Williams, 2005; Williams et al., 2007), so we dismiss ion exchange mechanisms involving smectite as a significant control on the Mg^{2+}/Ca^{2+} ratios of groundwaters and surface waters here. Instead, the slight differences observed between the watersheds could be related to the relative amounts of Silurian and Devonian carbonate rock, which have different proportions of dolostone relative to limestone lithologies, contributing to the glacial drift deposits. In addition, the sequence in which the soil waters contact calcite versus dolomite in systems open to CO_2 also influences the relative amounts of calcite and dolomite that can be dissolved at saturation (Palmer and Cherry, 1984).

Carbonate Speciation and Carbonate Mineral Equilibria

The soil zone in the shallow, porous glacial drift aquifers of the Tahquamenon, Cheboygan, and Huron watersheds provides an ample

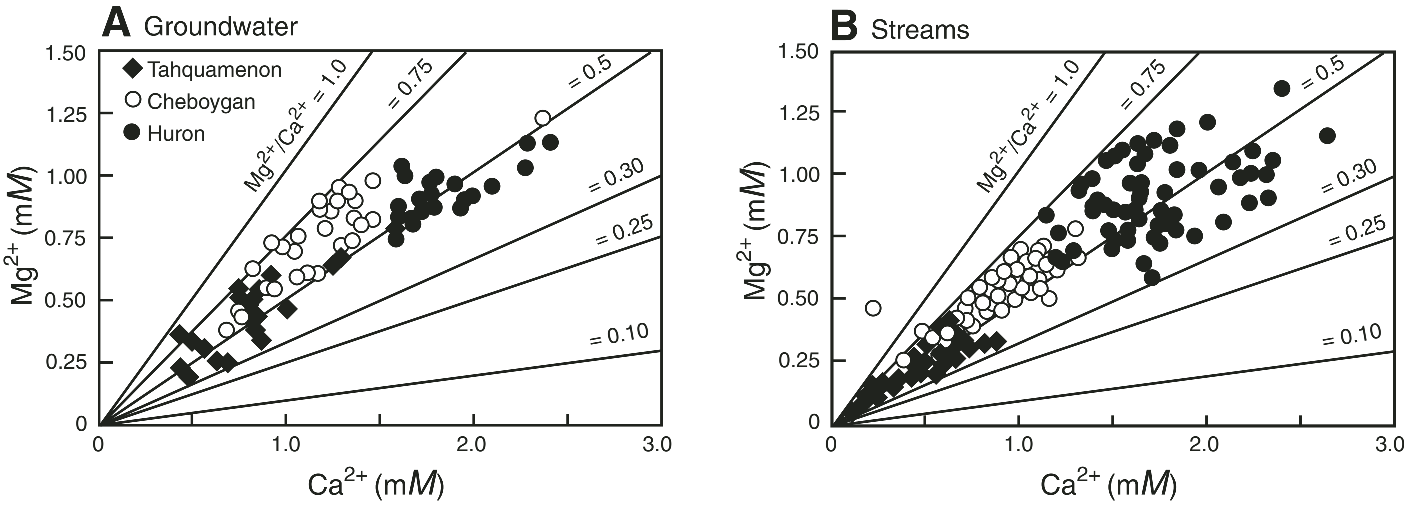

Figure 7. Mg^{2+} versus Ca^{2+} concentrations for groundwaters (A) and surface streams (B) within the three study catchments. The dissolution of both dolomite and calcite is evident from the high Mg^{2+} and Ca^{2+} concentrations and the high Mg^{2+}/Ca^{2+} ratios for the groundwaters and surface stream waters. The ratio 0.55 ± 0.13 indicates that about one mol of dolomite [as $CaMg(CO_3)_2$] dissolves for every 1 mol of calcite ($CaCO_3$) within the weathering zone of the watersheds.

supply of CO_2 for weathering in an open-system environment. The partial pressure of CO_2 within the groundwaters is at or below atmospheric P_{CO_2} of $10^{-3.5}$; however, the P_{CO_2} values differ significantly between the three watersheds (see summary values in Table 1) and reflect the differences in overlying vegetation and in the soil profile development with respect to amounts of carbonate minerals. The Huron watershed has P_{CO_2} values between $10^{-2.4}$ and $10^{-2.0}$, the Cheboygan has P_{CO_2} values ranging from $10^{-3.1}$ to $10^{-1.8}$, and the Tahquamenon watershed has the widest range of P_{CO_2} values, from $10^{-3.5}$ to $10^{-2.1}$. The Huron watershed has the longest growing season and more cropland than the other two watersheds, which can help to explain the higher P_{CO_2} values.

The variability in the $(IAP/K)_{calcite}$ values for the groundwaters from the three study watersheds is shown in Figure 8. The groundwaters within the three watersheds are at or near saturation for both calcite and dolomite. As shown in Table 1, calcite is on average ~1.5 times saturated in the groundwater, while dolomite is on average near equilibrium. Due to the solubility relations and the common ion effect (as shown in Fig. 2B), temperate soil water and groundwater that contact both calcite and dolomite are in theory capable of dissolving calcite to saturation and then continuing to dissolve dolomite, which remains undersaturated. If dolomite saturation is attained, then calcite must become supersaturated in the solution.

Because the groundwaters in our study are ~1.5 times supersaturated with respect to calcite and slightly undersaturated with respect to dolomite, this scenario requires that the dissolution kinetics of dolomite in groundwaters be more rapid than the precipitation kinetics of calcite. Near equilibrium for carbonate minerals, reaction rates of dissolution versus precipitation have very different kinetic rate laws such that dissolution is much more rapid than is precipitation at an equivalent departure from equilibrium (e.g., Walter, 1985; Blum et al., 1990). Thus, using saturation state averages for groundwaters in Table 1, it is not unreasonable to expect that dolomite dissolution rates at a ½ $IAP/K_{dolomite}$ value of 0.8 would be more rapid than calcite back precipitation rates in the same solution at a $IAP/K_{calcite}$ value of 1.3.

The saturation states with respect to calcite and calculated P_{CO_2} values for both groundwaters and related surface waters for the Tahquamenon, Cheboygan, and Huron watersheds are shown in Figures 9A, 9B, and 9C, respectively. The Tahquamenon surface waters have a wide range of P_{CO_2} values, from $10^{-1.8}$ to less than $10^{-3.5}$.

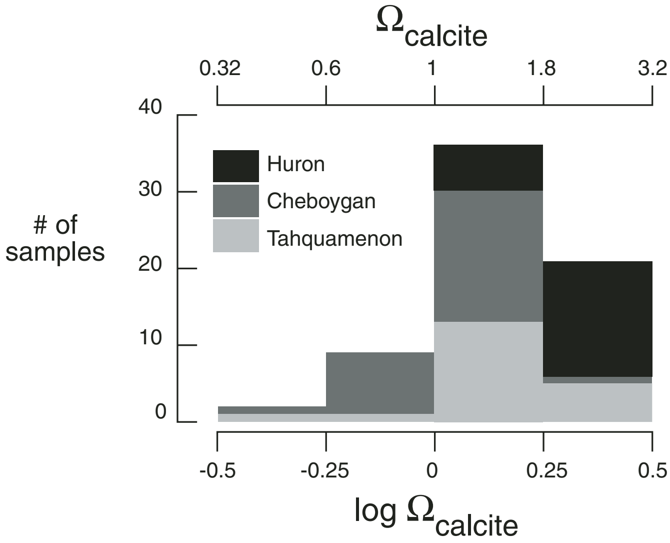

Figure 8. Ranges of groundwater calcite saturation states for each of the study three watersheds, shown as histograms. All three watersheds tend to have groundwaters that are slightly to significantly supersaturated for calcite and, thus, approach equilibrium with respect to more soluble dolomite.

These extremely low values are equivalent to the P_{CO_2} of the atmosphere. The average groundwater P_{CO_2} values differ significantly among the three watersheds (Tahquamenon: $10^{-2.96 \pm 0.36}$; Cheboygan: $10^{-2.45 \pm 0.30}$; Huron: $10^{-2.13 \pm 0.13}$).

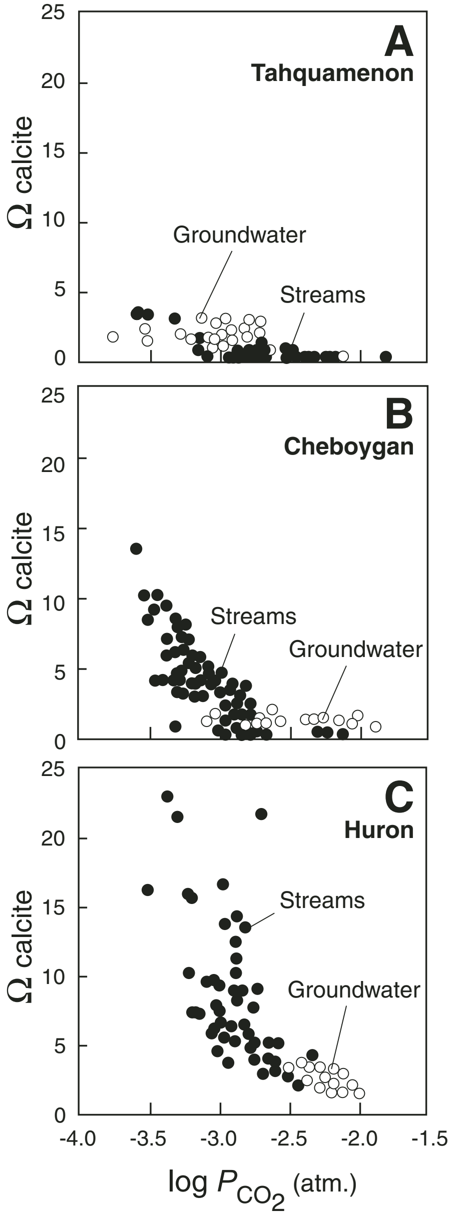

Figure 9. Plot of IAP/$K_{calcite}$ versus P_{CO_2} for surface waters relative to groundwaters for the three study watersheds. The Tahquamenon watershed (A) exhibits little difference in saturation state and P_{CO_2} for the groundwaters and surface waters. The Cheboygan surface waters (B) indicate a departure from the groundwater values and are approximately eight times saturated with respect to calcite. The Huron surface waters (C) are nearly 30 times saturated with respect to calcite.

The groundwaters are saturated with calcite at P_{CO_2} values much higher than that of the atmosphere. As this groundwater discharges to the surface, the gradient between the groundwater and the atmosphere facilitates the degassing of CO_2 from the water. Stream residence time and biologic activity also influence the loss of CO_2 from the stream water. This creates the conditions necessary for the increased saturation of calcite in the surface waters. The Huron watershed has the sharpest gradient between the P_{CO_2} value of the atmosphere and the groundwaters (see Fig. 9C). It also has the greatest degree of supersaturation for calcite in the surface waters. The Cheboygan watershed also has surface waters that are supersaturated for calcite, although not as highly supersaturated as the Huron (see Fig. 9B). The Tahquamenon watershed has only a few surface waters that are more saturated than the groundwaters; these are the waters that have lost CO_2 relative to the groundwater (see Fig. 9A). The degree of supersaturation with respect to calcite suggests that there may be losses of Ca^{2+} and HCO_3^- to carbonate reprecipitation along the stream drainage system.

Mass Balancing Dissolution and Precipitation: Mg^{2+}/HCO_3^- as Conservative Tracer

In principle, it should be possible to utilize the concentration relations between Ca^{2+} and HCO_3^- to examine losses due to calcite precipitation within stream reaches. However, tracking these changes in stream water chemistry is hampered by anthropogenic inputs to the surface water system. As discussed earlier, pollution from road salts adds excess Ca^{2+}, Na^+, and Cl^-, but not Mg^{2+} to surface waters, and this is particularly significant for the Huron watershed. The excess Ca^{2+} makes it an unreliable tracer of carbonate precipitation/dissolution. Instead, it is possible to utilize the amounts of Mg^{2+} and HCO_3^-, which are not a significant component of the anthropogenic salt load, to mass balance the amount of dissolution versus reprecipitation of carbonates in the surface water system. Importantly, only low-Mg calcite can precipitate if the saturation state increases via CO_2 loss, because dolomite precipitation is kinetically inhibited (e.g., Suarez, 1983; Kempe and Emeis, 1985; Komor, 1994). Thus, the Mg^{2+}/HCO_3^- ratio of surface waters relative to groundwaters provides a means of determining whether HCO_3^- has been lost via $CaCO_3$ precipitation (Mg^{2+}/HCO_3^- increases) or whether the water has simply been diluted by rainfall or concentrated by evaporation (Mg^{2+}/HCO_3^- remains constant).

The relationships between concentrations of Mg^{2+} and HCO_3^- in groundwaters and surface waters of the three watersheds are shown in Figure 10. The groundwaters have a fairly constant Mg^{2+}/HCO_3^- average ratio of 0.18, with a standard deviation of ±0.03 (see also Table 1 summary). This ratio proves to be a very useful quantity because it is determined in the groundwater, which is the major contributor of these ions to the streams. Because relatively small amounts of Mg^{2+} are removed during the precipitation of low-Mg calcite, the Mg^{2+}/HCO_3^- ratio can be used to compare differences between the initial groundwater chemistry and that of the more highly supersaturated surface waters.

The Tahquamenon and the Cheboygan surface waters all have the same Mg^{2+}/HCO_3^- molar ratio as the local shallow groundwater (see Fig. 10A). The relative constancy of the Mg^{2+}/HCO_3^- ratios of groundwaters and streams in these watersheds suggests that processes occurring within the streams do not significantly alter the early imprint of weathering zone values on carbonate weathering fluxes from dolomite and calcite. The surface stream waters from the Huron watershed have Mg^{2+}/HCO_3^- molar ratios (0.23 ± 0.05) that are higher than the groundwater ratio (see Tables 1 and 2; Fig. 10B). The relative loss of HCO_3^- can be attributed to localized precipitation of calcium carbonate within lake and wetland systems within the Huron watershed. A more detailed discussion of the sites of carbonate precipitation in the Huron from the headwater to downstream reaches is provided in Szramek and Walter (2004). Importantly, the net effect of calcite precipitation on riverine carbonate weathering fluxes from the Huron is small because precipitation is only evident at lowest discharge conditions (Szramek et al., 2007).

Comparisons with North American Drainage: Divalent Cation and Inorganic Carbon Budgets

The results obtained from our study of surface water and groundwater geochemistry in three diverse watersheds established on glaciated landscapes of the mid-continent region can be placed in a larger context through comparison to their larger drainage systems. The two most significant rivers draining the North American continent are the Mississippi and St. Lawrence Rivers. As shown on the drainage basin map for these rivers (see Fig. 1), a significant amount of the drained region has been recently glaciated and is largely in contact with glacial drift deposits. Average composition and annual water and elemental fluxes were obtained for the Mississippi and St. Lawrence River basins. Data for each of the main reaches of the Mississippi (Missouri, Upper Mississippi, Ohio, Tennessee, Arkansas, and Red Rivers) and for the three Michigan study watersheds (Tahquamenon,

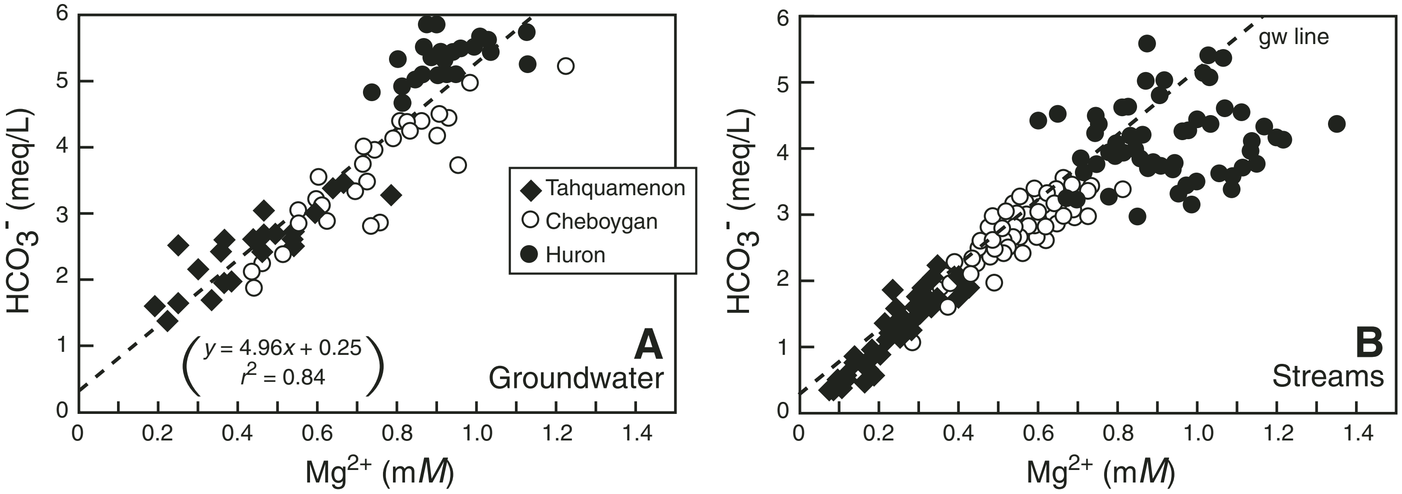

Figure 10. Mg^{2+} versus HCO_3^- concentrations for groundwaters (gw) (A) and surface stream (B) waters in the three study catchments. Groundwaters from all three watersheds have a similar Mg^{2+}/HCO_3^- ratio value, as shown by the regression equation. Both the Cheboygan and Tahquamenon watersheds have Mg^{2+}/HCO_3^- ratios in surface waters comparable to their respective shallow groundwaters. The Huron watershed has a ratio that has increased relative to the source groundwater, indicating likely back precipitation of low-Mg calcite in the lower reaches of the Huron River.

Cheboygan, and Huron) were obtained from the USGS–National Stream Quality Accounting Network (NASQAN) database (Alexander et al., 1998) using compiled data on average river discharge (in L yr^{-1}), water chemistry (Mg^{2+}, Ca^{2+}, HCO_3^- concentrations), and drainage basin area (km^2). Data on average discharge and chemical composition for the mouth of the St. Lawrence River were obtained from Hélie et al. (2002) and Rondeau et al. (2005).

The relations between Ca^{2+} and Mg^{2+} concentrations for the various river drainages are shown in Figure 11 along with the value for world average river water (data from Berner and Berner, 1996). All of these North American river drainages have higher Mg^{2+} and Ca^{2+} concentrations than world average river water. The Mg^{2+}/Ca^{2+} ratios in all these rivers fall within a range of values between 0.30 and 0.75, indicating that dolomite and calcite weathering contribute subequal proportions of these divalent cations. The budgets for water, HCO_3^-, and Mg^{2+} annual fluxes from the main North American river drainages are shown in Figure 12. The contributions of watersheds that fall within the recently glaciated region of North America (St. Lawrence, Upper Mississippi, Ohio, and Missouri Rivers) show that these are disproportionately large for both Mg^{2+} and HCO_3^- budgets.

Taken together, these comparisons show that dolomite and calcite weathering are both important contributors to riverine solute budgets and that temperate, recently glaciated watersheds are disproportionately large contributors to carbonate weathering fluxes. Increased global temperature is widely considered to be a control on silicate mineral weathering rates in geochemical models (e.g., Berner et al., 1983; Bluth and Kump, 1994). The comparisons made here show that contributions from carbonate mineral weathering, and especially the relative proportions of dolomite relative to calcite weathering, can actually increase with decreasing temperature.

SUMMARY AND CONCLUSIONS

The suite of geochemical analyses obtained on the surface waters and shallow groundwaters of the Tahquamenon, the Cheboygan, and the Huron watersheds in the U.S. mid-continent demonstrates a remarkable regularity in the

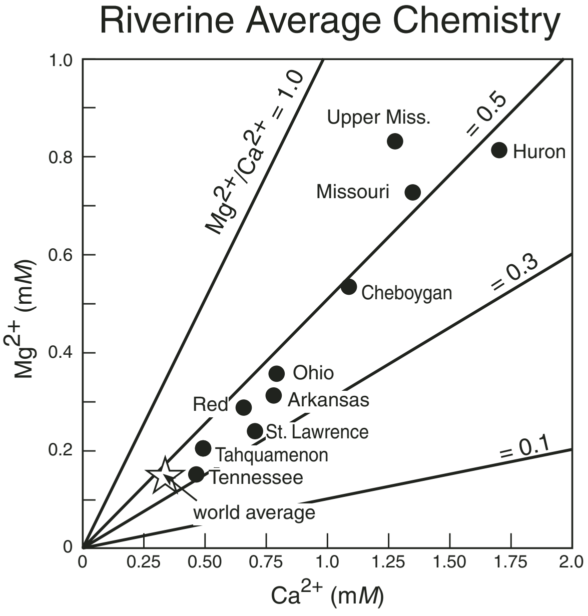

Figure 11. Average Mg^{2+} versus Ca^{2+} concentrations for the three study watersheds in Michigan (Tahquamenon, Cheboygan, and Huron) versus average values for the mouth of the St. Lawrence River and Mississippi River tributaries (Ohio, Upper Mississippi, Missouri, Ohio, Tennessee, Red, and Arkansas Rivers). The composition of world average river water is also indicated.

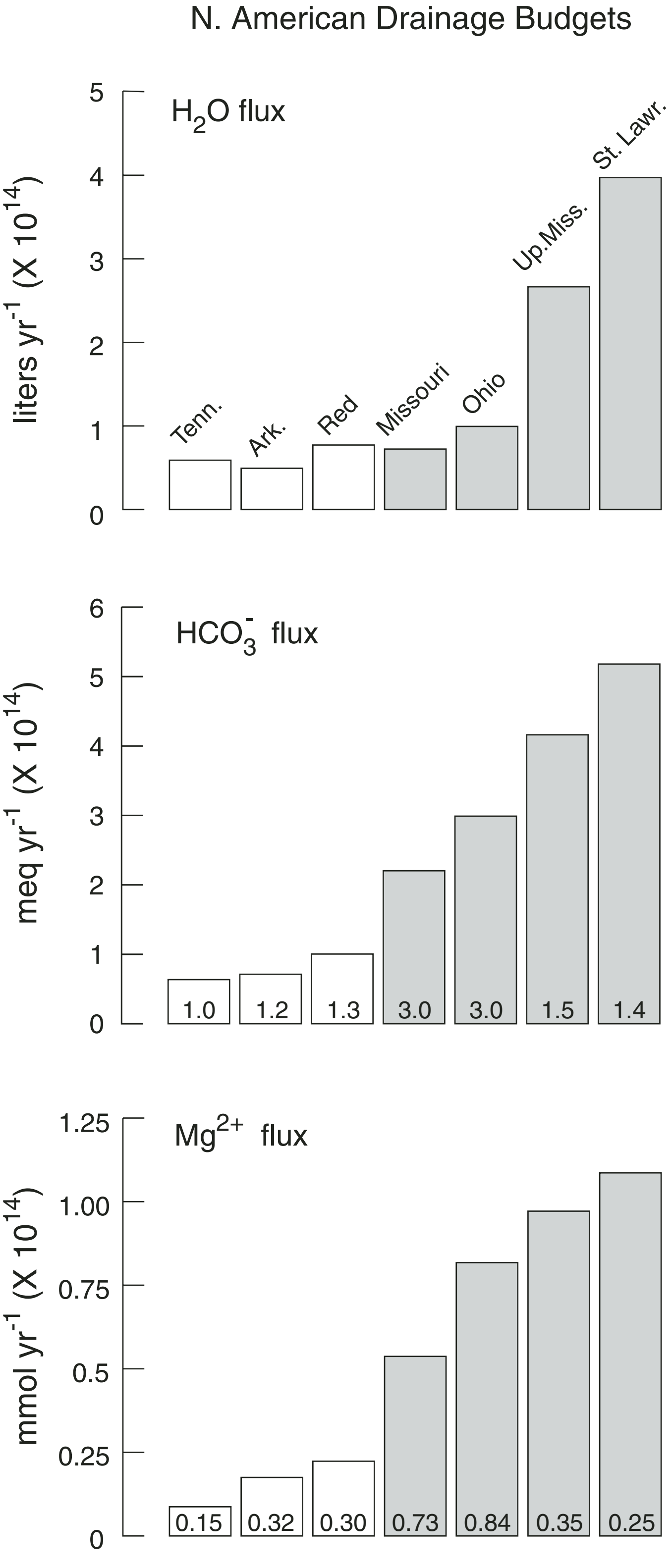

Figure 12. Annual drainage budgets for the St. Lawrence and tributaries of the Mississippi River for water, HCO_3^-, and Mg^{2+} fluxes. Tributaries within the extent of Pleistocene glaciation (see Fig. 1) are indicated by shaded bars in each histogram. The numbers within the histograms for HCO_3^- and Mg^{2+} represent the average concentration of the respective species in each of the tributaries. The trends indicate that most of the Mg^{2+} and HCO_3^- fluxes from the main North American drainage systems are derived from temperate, glaciated watersheds.

parameters controlling the dissolved inorganic carbon mass balance within these watersheds. Despite their large spatial separation and different glacial histories and types of glacial drift, groundwaters from all three watersheds in Michigan have a very consistent Mg^{2+}/HCO_3^- mole ratio value of ~0.2. The differences in average HCO_3^- value of shallow groundwaters are controlled by equilibrium with respect to different P_{CO_2} values. Surface water Mg^{2+} and HCO_3^- concentrations for the Cheboygan watershed are very close to those of the shallow groundwaters, while those from Tahquamenon and Huron watersheds tend to be lower than their respective groundwaters, likely because of groundwater dilution by runoff.

Because of the local use of $CaCl_2$ de-icing salts (Jones and Sroka, 1997), Ca^{2+} concentrations are poor indicators for carbonate dissolution or precipitation mass balances. Instead, the relatively constant value of the Mg^{2+}/HCO_3^- ratio of groundwaters can be used to evaluate changes in surface waters due to calcite back precipitation. The only surface streams that have markedly different Mg^{2+}/HCO_3^- ratios from groundwaters are in the Huron watershed, where HCO_3^- appears to have been selectively removed by carbonate precipitation. However, even in the Huron watershed, the net effect of calcite precipitation on riverine carbonate weathering fluxes is small because calcite precipitation is only evident at lowest discharge conditions (Szramek et al., 2007).

The degree of calcite saturation and P_{CO_2} values calculated for surface waters and groundwaters also show significant differences among the three watersheds. Both the Cheboygan and the Huron watersheds have groundwaters that are ~1.6 times saturated with respect to calcite and near equilibrium with respect to dolomite, at different subsurface P_{CO_2} values. Stream and river waters in both watersheds have evolved to higher calcite saturation states. However, the Huron River has evolved to a much higher degree of calcite supersaturation, generally between 8 and 10 times supersaturated. The range of Mg^{2+}/Ca^{2+} values observed in groundwaters and surface waters of the three study watersheds in Michigan suggests that dolomite and calcite dissolution contribute subequally.

We suggest that the increase in the relative and absolute solubility of dolomite relative to calcite at temperatures below 30 °C plays an important role in regulating the weathering fluxes of these two minerals. Comparisons among the main North American river drainages support this contention, showing that both Mg^{2+} and HCO_3^- riverine concentrations and annual fluxes are heavily weighted toward drainages located in the temperate, glaciated portion of the continent. The lack of significant modification of inorganic carbon fluxes by back precipitation in surface waters is also an important characteristic of these watersheds.

These results have significance in terms of the short- and long-term carbon cycle and the role played by carbonate mineral weathering. In the short term, the likely increases in the size of the terrestrial and atmospheric carbon pools due to fossil-fuel burning would be expected to increase carbon cycling rates in soils and, hence, weathering zone P_{CO_2} values. Carbonate mineral weathering fluxes to surface waters and shallow groundwaters should increase, with influence on both surface water chemistries and on global fluxes to the ocean reservoir.

Although carbonate mineral weathering is generally considered unimportant in long-term carbon cycle models, the significant role of dolomite weathering suggested here may require revision of that assumption. Dolomite is widely known to have been much more common as a primary marine mineral in other geologic time periods (e.g., Holland and Zimmermann, 2000). Today, dolomite weathering on continents produces HCO_3^- that cannot be balanced by dolomite precipitation in modern oceans. Thus, asymmetry of the Ca^{2+} and Mg^{2+} sources during weathering on continents (dolomite and calcite weathering) and the fate of the resultant HCO_3^- in the marine environment (calcite versus dolomite precipitation) merit additional study.

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